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Field Screening for Heavy Metals with Portable XRF Units

R. G. McCain
S. J. Guzek

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Westinghouse Hanford Company
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Richland, Washington 99352

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II. Author's Name: Mr. R. G. McCain, MSIN H4-55
Westinghouse Hanford Company
P. O. Box 1970
Richland, WA 99352

III. Co-Author's Name(s): S. J. Guzek
Westinghouse Hanford Company

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Lead Author	Phone	MSIN	Other Author(s) or Requestor
R. G. McCain	6-0777	H4-55	S. J. Guzek
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FIELD SCREENING FOR HEAVY METALS WITH PORTABLE XRF UNITS

R.G. McCain & S.J. Guzek
Westinghouse Hanford Company
P.O. Box 1970
Richland, Washington 99352
(509) 376-0777

ABSTRACT

Portable X-Ray Fluorescence (XRF) units are available for sample analysis or in situ measurement of heavy metals. In many field screening applications, it is sufficient to identify samples or areas in which contamination is present. This paper presents a new approach that provides a qualitative indication of heavy metal content with minimal sample preparation and data evaluation. In the "scan" approach, a portable XRF unit is configured to report the integrated gross count rate for each of several contiguous energy bands. Detection of heavy metal contaminants is based on comparison of gross count rates in each energy band with corresponding background levels from material with a similar matrix.

INTRODUCTION

In many field screening applications, a primary question is the nature and extent of contamination. Although accuracy and sensitivity are important, the time required to obtain results can be an overriding concern. Decisions relating to sample collection and disposition, interim designation of waste materials, or worker health and safety must often be made in a very short time without recourse to laboratory analytical results.

The overall quality of the sampling and analysis program can be greatly enhanced if samples collected for laboratory analysis are obtained with some knowledge of the range and spatial distribution of contaminant levels. Proper management of waste materials is facilitated when data regarding waste constituents are provided promptly. Worker health and safety are improved when contaminants present at a site are identified quickly allowing modification of the worker protection or site monitoring requirements where appropriate. During remediation or removal of contamination, the quantity of material to be treated and/or disposed can be greatly reduced if the presence of contamination can be determined on a real-time basis.

In these cases, it can be sufficient to identify samples or areas in which contamination is present. In this context, contamination can be defined as concentrations significantly above background levels. Also, it is not always necessary to provide specific identification of the contaminant involved.

Elements such as lead, arsenic, cadmium, chromium, zinc, mercury, and copper are frequently cited as contaminants of concern in soils at hazardous waste sites. These elements can be detected using XRF methods. In contrast to other instrumental methods of heavy metal analysis such as inductively coupled plasma spectroscopy (ICP) or atomic absorption (AA), XRF methods offer greater potential for field application. In particular, energy dispersive (ED) XRF systems offer the capability to detect and quantify a wide range of elemental contaminants with minimal sample preparation. In recent years, small portable ED-XRF units have become commercially available. These instruments generally consist of a probe unit with one or more gamma-emitting radioisotope sources and a detector, connected to a battery-powered electronics package which contains a high voltage power supply for the detector, multichannel analyzer, and associated electronics and microprocessors. Portable ED-XRF units are necessarily limited in their capability to excite and resolve characteristic XRF energy lines, but they offer the capability for quick field measurements. These instruments can also be used to make in situ measurements on soil, concrete, asphalt, or other surfaces.

FIELD SCREENING WITH PORTABLE ED-XRF UNITS

The use of portable ED-XRF units for field screening is not new. These instruments have been used to make field measurements in metallurgy, mining, and other fields. The Environmental Protection Agency (EPA) has identified portable XRF as a field screening technique and discussed its use to screen for lead contamination at a hypothetical superfund site in the guidance documents related to development and implementation of Data Quality

Objectives (DQOs)[1]. Numerous papers describing the use of portable ED-XRF units in field screening of heavy metal contamination have been presented. The principles of XRF as applied to waste analysis are discussed by Kendall[2]. A summary of the concept of field screening with portable XRF units is provided by Raab et al.[3]

Portable ED-XRF units are generally designed to provide a numeric output for several elements of interest. The instrument used to generate the data in this paper is the X-Met 880*, manufactured by Outokumpu Electronics, Inc. The X-Met 880 is designed to operate in either an identify 'ID' mode or an assay 'ASSAY' mode. Each measurement mode is stored as a user-defined model in the instrument memory. The X-Met can maintain up to 32 models in memory. In the ID mode, the instrument compares data from unknowns with those from standards and identifies the best match, if any. This mode is designed primarily for alloy identification, and will not be discussed further. In the ASSAY mode, the X-Met 880 measures count rates for up to ten elements, applies peak overlap corrections, and provides up to six numeric outputs which are defined in terms of the corrected measurement values. Available outputs include the gross count rates, net (deconvoluted) count rates, assay values, and standard deviation (counting error) of the assay values. The ASSAY models are developed by first specifying the parameters to be measured. The instrument requests a measurement of the appropriate pure element spectra or recalls it from memory--these spectra are used to compute measurement ranges and peak overlap factors. The user then specifies the dependent outputs and measures a suite of calibration samples that contain a range of the elements of interest in a matrix similar to that in which measurements are to be made. During model development, the user specifies relationships between dependent (assay) outputs and the independent (net count rate) values. The X-Met computes the regression for each postulated relationship and stores the result. By evaluation of the regression statistics, the best relationship is selected and stored in the model parameters. This process is repeated for each of the six assay values. Ideally, this empirical calibration approach accounts for major interelement and matrix effects. However, the empirical calibration process requires a suite of calibration samples with similar matrix characteristics that have been spiked with a range of concentrations of each element of interest. If six assay values are to be determined, as many as twenty to thirty calibration samples could be required. In many field screening applications, however, such a suite of calibration samples might not be available, or the contaminants of concern could be poorly defined. It is not always possible to use samples from previous projects as calibration samples, because matrix conditions can be different and the required analytes might not be present at appropriate concentration levels.

To take a measurement in the field, the operator selects the appropriate model from the X-Met front panel or computer interface, places the probe against the sample or surface to be measured and pulls the trigger. After the counting time is completed, the X-Met displays the six assay values on the front panel display. At this point, the net count rates and gross count rates can also be displayed by issuing simple commands from the X-Met front panel or computer interface, and the spectra may be downloaded for viewing and/or plotting. However, examination of these parameters or viewing of the spectra will require a portable computer. While such computers are available, their use in the field greatly restricts the mobility of the X-Met, and increases overall measurement and data evaluation time. What is needed is a means to make a determination regarding the presence of heavy metal contamination based on evaluation of the six assay values available from the X-Met front panel display. This has led to the development of "scan" models.

THE SCAN MODEL

The "scan" model concept is based on the observation that materials with similar matrix characteristics and element concentrations should exhibit similar XRF spectra under similar measurement conditions, assuming source energy and intensity remain the same. The integrated "background" count values for a given channel range should be similar for all uncontaminated sands, and a contaminated sand should exhibit an increased count rate in those channels which correspond to the position of the energy peak(s) associated with the contaminants.

Because the X-Met can report assay values for as many as six elements, each scan model consists of assay output for six contiguous bands over the useful range of the spectra. Each independent measurement is designated by the elemental symbol for an element whose major peak falls within that range. This is done because the X-Met will only accept elemental symbols (and BS for backscatter) as valid independent names. Measurement limits are manually defined such that commonly encountered peaks are recorded as an independent; however, counts in each channel within the range are incorporated, without regard to the location of actual element peaks. The internal deconvolution function of the X-Met is side-stepped by manually setting the "G-matrix" or peak overlap factors (1.0 on the diagonal, and

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*X-Met is a trademark of Outokumpu Electronics, Inc.

0 elsewhere). This means that the pulse frequencies (gross count rates) and channel intensities (net count rates) reported by the X-Met are equal, i.e., no deconvolution is performed. (The instrument automatically accumulates total counts over the specified range and divides by measurement time to provide an output in counts per second.) The modelling capability of the X-Met is used to define six assay outputs, or dependents, where each dependent is a function of only one independent, with an intercept of 0 and a slope of 1.0. The net effect is that the assay output is the gross count rate for each band. It is not necessary that the name of the assay output be an element symbol. Figures 1 and 2 show a typical background spectra and illustrate the scan model concept applied to measurements made with the Am^{241} and Cm^{244} sources. Table 1 lists the energy ranges for each assay output.

The assay outputs for a "background" or uncontaminated sample represent baseline values. Assay outputs from an unknown sample can be compared to these values: if a significant difference is found in one or more bands, it may indicate the presence of an anomalous amount of an element whose characteristic XRF peak falls within that part of the energy spectrum. If a sufficient number of background samples are available, statistical procedures can be applied to determine a confidence interval for each mean background value. Assay values outside these confidence intervals are then interpreted as indications of anomalies that warrant further evaluation, which could include examination of the XRF spectra and/or laboratory analysis. Table 2 lists background assay values for a wide range of samples analyzed as part of a site-wide background study.

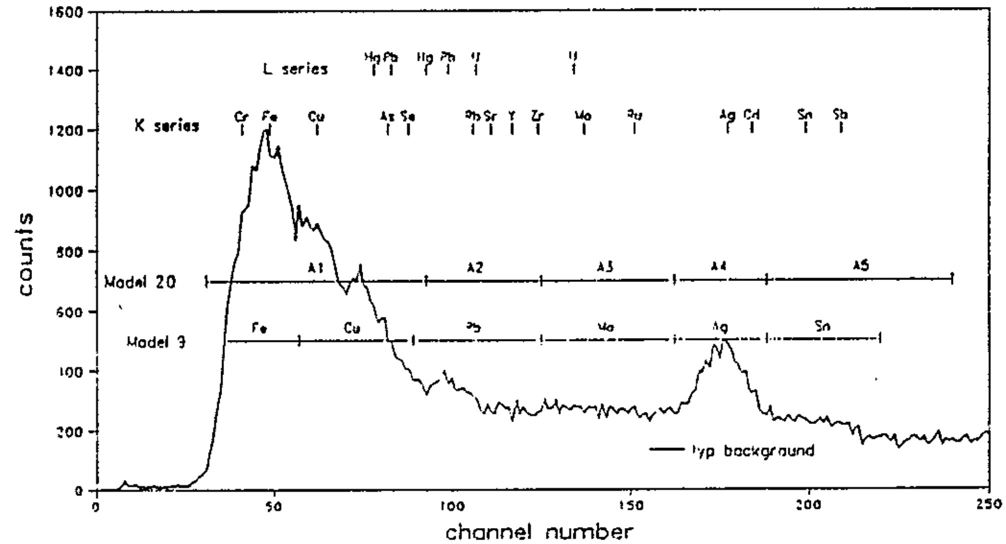

Figure 1. X-MET 880 Scan Models (Am-241 source).

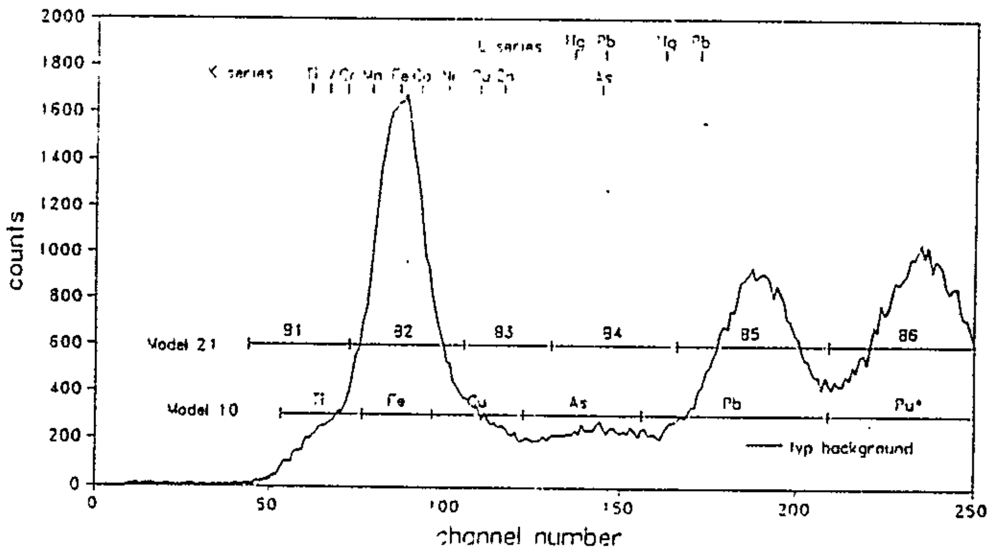

Figure 2. X-MET 880 Scan Models (Cm-244 source).

Table 1. X-MET 880 Scan Models.

Model 9: "ASCAN" (Am^{241} source)

Assay	Channels	Energy (KeV)	Elements
Fe	36 - 56	4.8 - 7.3	Cr, Mn, Fe, Co
Cu	57 - 88	7.3 - 11.3	Ni, Cu, Zn, As, Se, Hg, Pb
Rb	89 - 124	11.3 - 15.8	Br, Rb, Sr, Y, Zr, Hg, Pb, U
Mo	125 - 161	15.8 - 20.5	Mo, Ru, U
Ag	162 - 188	20.5 - 23.8	Ag, Cd
Sn	189 - 220	23.8 - 27.8	Sn, Sb

Model 20: "ASCAN1" (Am^{241} source)

Assay	Channels	Energy (KeV)	Elements
A1	31 - 92	4.1 - 11.8	Cr,Mn,Fe,Co,Ni,Zn,As,Se,Hg,Pb
A2	93 - 124	11.8 - 15.8	Br, Rb, Sr, Y, Zr, Hg, Pb, U
A3	125 - 161	15.8 - 20.5	Mo, Ru, U
A4	162 - 188	20.5 - 23.8	Ag, Cd
A5	189 - 240	23.8 - 30.3	Sn, Sb
BS	255	> 32	backscatter

Model 10: "BSCAN" (Cm^{244} source)

Assay	Channels	Energy (KeV)	Elements
Ti	53 - 75	4.0 - 5.6	Ti, V, Cr, Ba
Fe	76 - 96	5.6 - 7.2	Mn, Fe, Co
Cu	97 - 121	7.2 - 8.9	Ni, Cu, Zn
As	122 - 155	8.9 - 11.4	As, Se, Hg, Pb
Pb	156 - 209	11.4 - 15.3	Rb, Sr, Y, Hg, Pb
Pu	210 - 254	15.3 - 18.5	scattering, absorption

Model 21: "BSCAN1" (Cm^{244} source)

Assay	Channels	Energy (KeV)	Elements
B1	44 - 71	3.4 - 5.4	Ti, V, Ba
B2	72 - 104	5.4 - 7.7	Cr, Mn, Fe, Co, Ni
B3	105 - 129	7.7 - 9.5	Cu, Zn
B4	130 - 165	9.5 - 12.1	As, Se, Hg, Pb
B5	166 - 208	12.1 - 15.2	scattering/absorption of secondary X-rays
B6	209 - 254	15.2 - 18.5	

Table 2. X-MET 880 Scan Models
Summary of Site-Wide Background Values.

Model 9: "ASCAN" — 126 samples

	Fe	Cu	Rb	Mo	Ag	Sn
mean	397.7	342.2	188.4	149.6	145.9	102.8
stdev	33.6	7.2	10.2	4.3	4.8	3.4
min	330.7	320.9	168.3	139.9	134.6	95.15
max	475.6	359.7	211.6	161.5	159.4	112.9

Model 10: "BSCAN" — 126 samples

	Ti	Fe	Cu	As	Pb	Pu
mean	134.7	774.0	188.9	122.8	422.1	463.0
stdev	24.0	210.1	25.7	9.2	50.0	53.1
min	90.4	387.4	141.1	111.5	336.3	359.8
max	188.9	1281	252.4	158.8	538	575.6

Model 20: "ASCAN1" — 114 samples

	A1	A2	A3	A4	A5	BS
mean	781.4	163.9	149.8	146.0	154.7	1762.3
stdev	33.6	9.1	4.2	4.8	5.2	62.7
min	688.2	146.2	139.9	134.6	144.0	1600.8
max	847.7	185.2	161.5	159.4	168.8	1912.4

Model 21: "BSCAN1" — 114 samples

	B1	B2	B3	B4	B5	B6	BS
mean	88.9	946.2	110.3	128.2	376.3	464.8	813.1
stdev	13.2	241.0	3.8	11.1	44.6	52.1	15.8
min	64.7	511.4	101.6	116.2	299.6	365.0	777.9
max	120.7	1518.8	118.0	173.8	488.6	582.7	849.4

APPLICATION OF THE SCAN MODEL

In August, 1991, an expedited response action (ERA) was carried out at the 300 Area process trenches to remove uranium contaminated sediments. In conjunction with this effort, the X-Met 880 was used on an experimental basis to investigate the feasibility of the scan model concept. A series of in situ measurements were made along the bottom of the west trench, and along one section up the side slope of the trench. These measurements were made before any sediments were removed, and again after the contaminated soils were removed. In this case model 9 was used and index values were stored in a small battery operated data logger. In this trench, the primary contaminants were uranium, zirconium and copper deposited by waste water from nuclear fuel processing operations. For uranium, the characteristic energy lines detectable by the X-Met would be the L_α and L_β lines at 13.613 and 17.218 KeV, respectively. For the Am^{241} source, these lines would center on channels 107 and 134. For Zirconium, the detectable characteristic energy line would be the K_α at 15.774 KeV, which corresponds to channel 124. For model 9 (see Figure 1 and Table 1), channels 107 and 124 fall within the Rb range, and channel 134 falls within the Mo range. Hence, elevated levels of either uranium or zirconium would be expressed as anomalous values in the Rb index value. The U L_β peak at channel 134 would also contribute to elevated values of the Mo index. Because the Zr peaks occurs at the boundary between the Rb and Mo ranges, elevated Zr will also result in elevated Mo index values. This is illustrated in Figure 3, which shows a typical contaminated soil spectra superimposed on a background spectra. The dotted lines show the respective index values. Note that the uranium and zirconium peaks are expressed as significant differences in the Rb and Mo index values.

Figure 4 shows the Rb index data for a profile down the center of the trench. The mean background value is based on measurements from similar soils obtained from a nearby undisturbed location. Note that in situ values observed in the trench prior to the ERA are considerably elevated relative to background, whereas measurments made after the contaminated soil was removed indicate approximate background values.

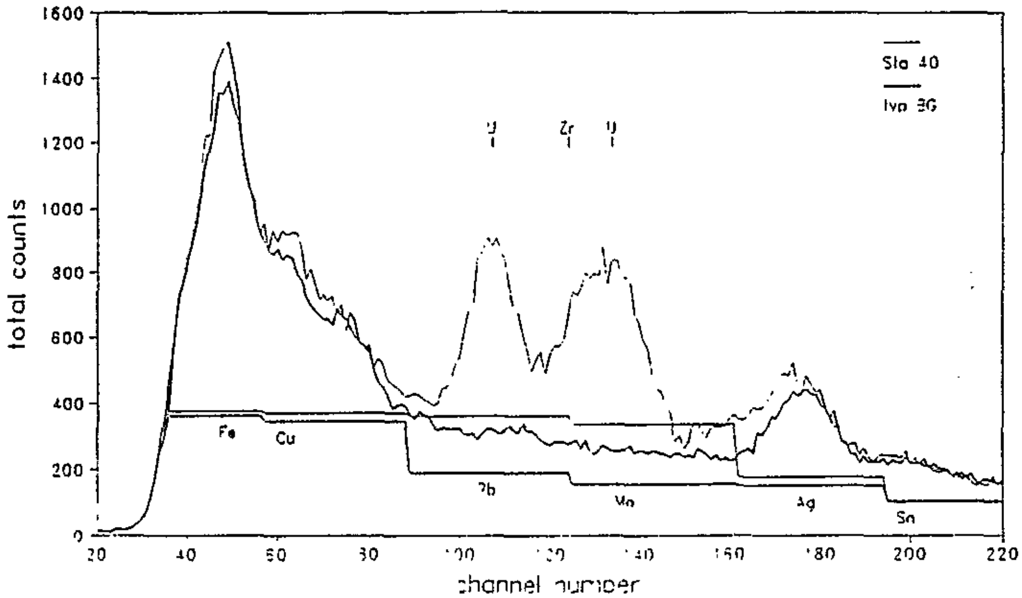

Figure 3. 316-5 Process Trenches, West Trench
(In Situ XRF Spectra, Am-241, 60 sec).

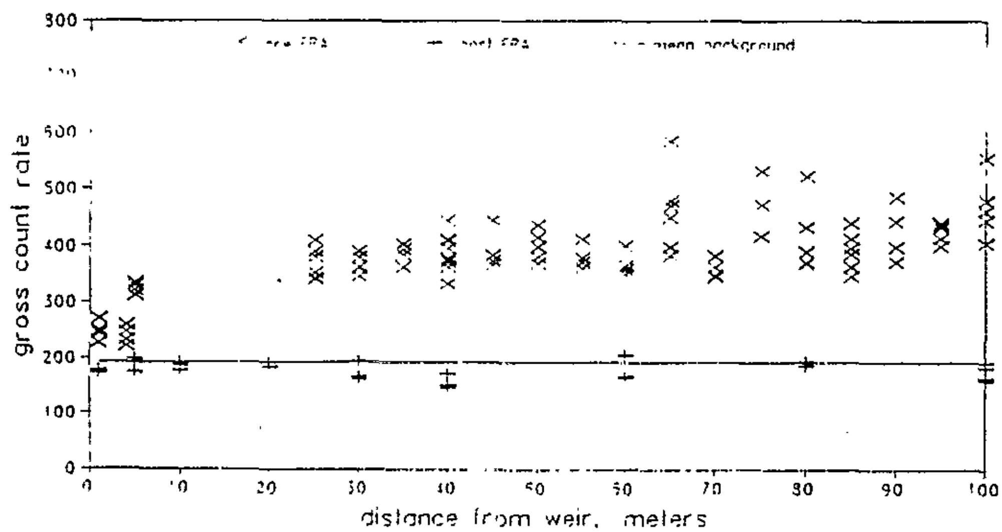

Figure 4. West Process Trench
(Model 9, "ASCAN": Rb Index Values).

CONCLUSIONS

Available data suggest the scan approach can be used with a portable ED-XRF unit such as the X-Met 880 to detect anomalous levels of heavy metal contamination in soils or other surfaces. This approach allows the operator to make a simple measurement and provides criteria for the rapid evaluation of contamination potential, without recourse to spectral display and extensive data evaluation. Obviously, this approach is somehat limited, because detection limits are necessarily somewhat high.

REFERENCES

1. Environmental Protection Agency, Data Quality Objectives for Remedial Response Activities; Example Scenario: RI/FS Activities at a Site with Contaminated Soils and Ground Water, EPA/540/G-87/004, Environmental Protection Agency, Office of Emergency and Remedial Response, Hazardous Site Control Division, Washington, D.C. (1987).

2. D. S. KENDALL, "The Application of X-Ray Fluorescence Spectrometry to the Analysis of Hazardous Wastes" in M. S. SIMMONS (editor), Hazardous Waste Measurements, Lewis Publishers, Chelsea, Michigan (1991).

3. G. C. RAAB, R. E. ENWALL, W. H. COLE, III, M. L. FABER, AND L. A. ECCLES, "X-ray Fluorescence Field Method For Screening of Inorganic Contaminants at Hazardous Waste Sites" in M. S. SIMMONS (editor), Hazardous Waste Measurements, Lewis Publishers, Chelsea, Michigan (1991).

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R.G. McCain & S.J. Guzek
Environmental Remedial Action Group
Westinghouse Hanford Company
P.O. Box 1970
Richland, WA 99352

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Boise, ID
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Three Levels of Analytical Requirements for Metals[1]

Level	Degree of Analytical Requirement			Purpose
	precision	accuracy	IDL	
1 (IV)	± 5%	± 10%	ppb	Litigation and regulatory enforcement
2 (III)	± 10%	± 15%	ppm	Evaluate and assess average pollutant exposure to humans and animals
3 (I, II)	± 10%	± 50%	≤ 1000ppm	Screening, preliminary evaluation and on-site decision- making

1 Raab, G.A.; D. Cardenas; S.J. Simon & L.A. Eccles (198?); " Evaluation of A Prototype Field-Portable X-Ray Fluorescence System for Hazardous Waste Screening"

Factors Affecting Interpretation of XRF Data

- Source energy level and excitation efficiency
- Detector efficiency and energy resolution capability
- Measurement time
- Matrix effects:
    - Scattering
    - Absorption
- Interelement effects:
    - Peak overlap
    - Secondary excitation
    - Secondary absorption

X-Met 880
Analytical Methods

ID Model

- Instrument attempts to find match based on comparison of relative intensities. Output is identification of material.

- Primarily used to identify metal alloys. May also be useful in stratigraphic correlation, and in monitoring cleanup activities.

ASSAY Model

- Instrument computes assay values from XRF intensities based on empirical calibration.

- Types of ASSAY Models

  - ASSAY: Output is in concentration values, with empirical calibration based on regression to to 20-30 calibration standards. Provides quantitative output.

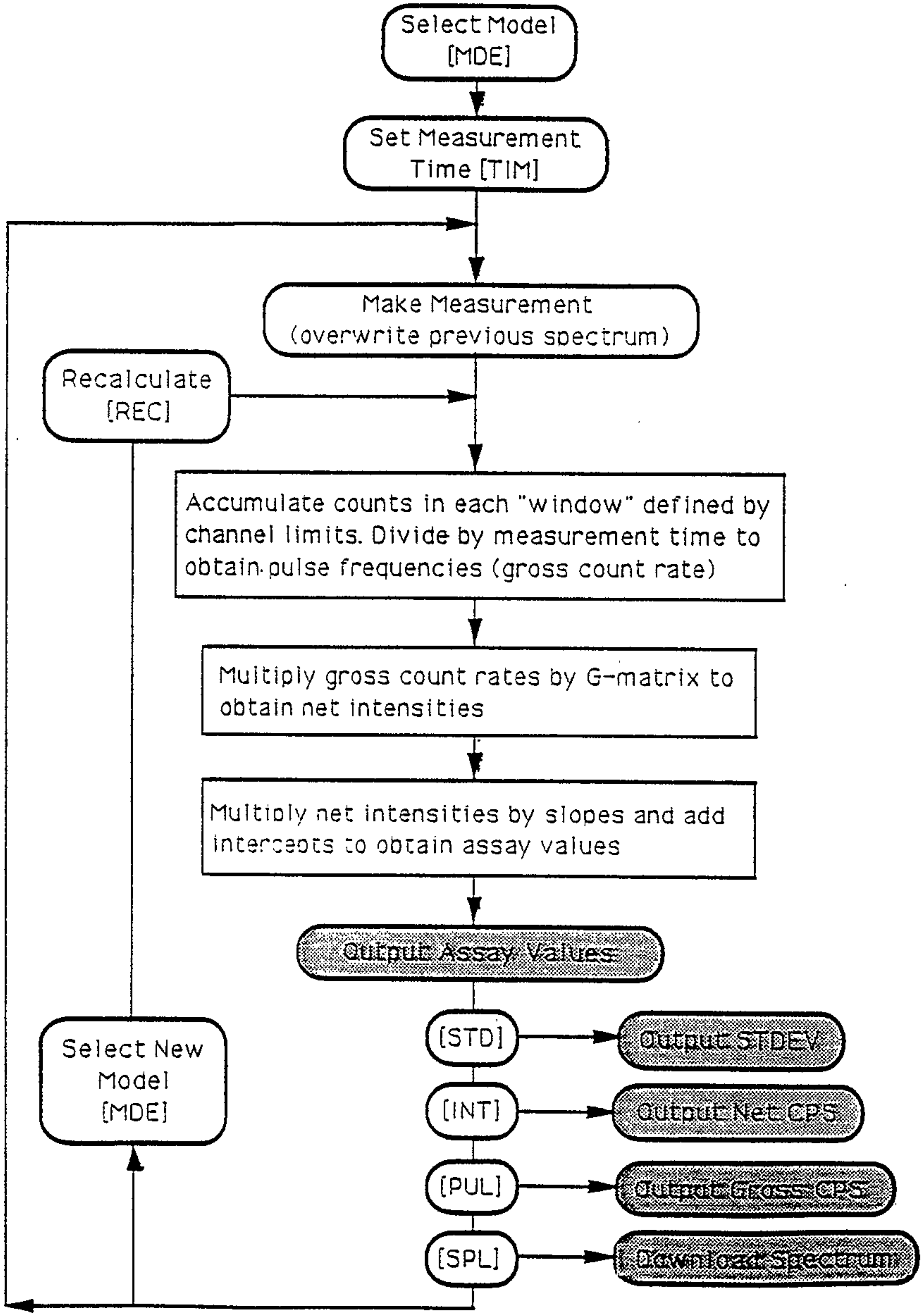
  - INDEX: Output is in net intensity for each element of interest. Provides qualitative output.

  - SCAN: Output is gross count rate for six elements which represent adjacent bands over the useful part of the spectrum. All channels within the useful part of the spectrum are accumulated into one of the element bands. Provides a non-specific indication of the possible presence of contamination

Spectral Evaluation

- Download and evaluate spectra

- Comtamination detected by comparison of spectra to background. Elements identified by energy level



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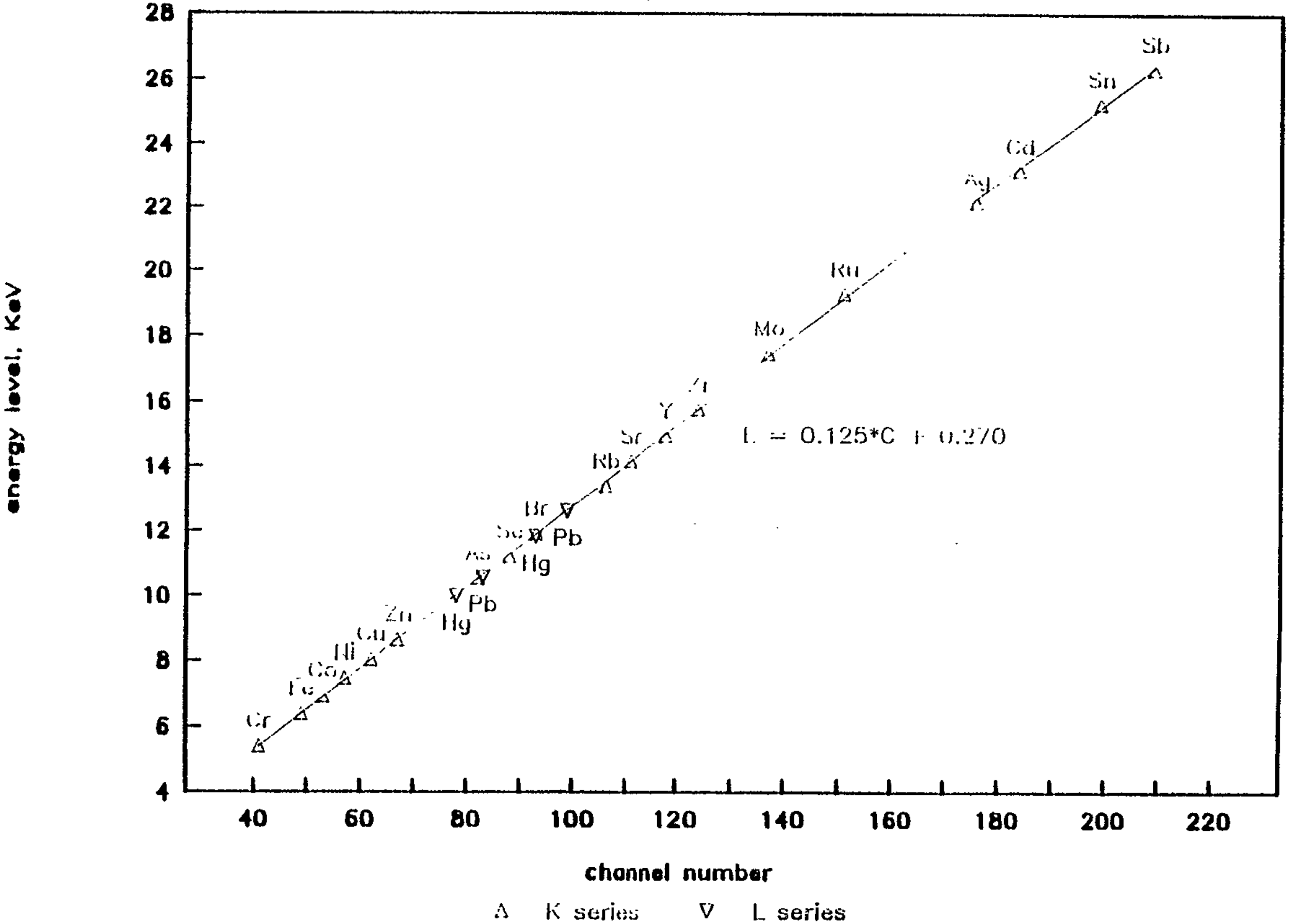
9 3 1 2 7 6 3 1 0 7 9

Energy Levels and Channel Numbers

X-Met 880, Am 241 Source



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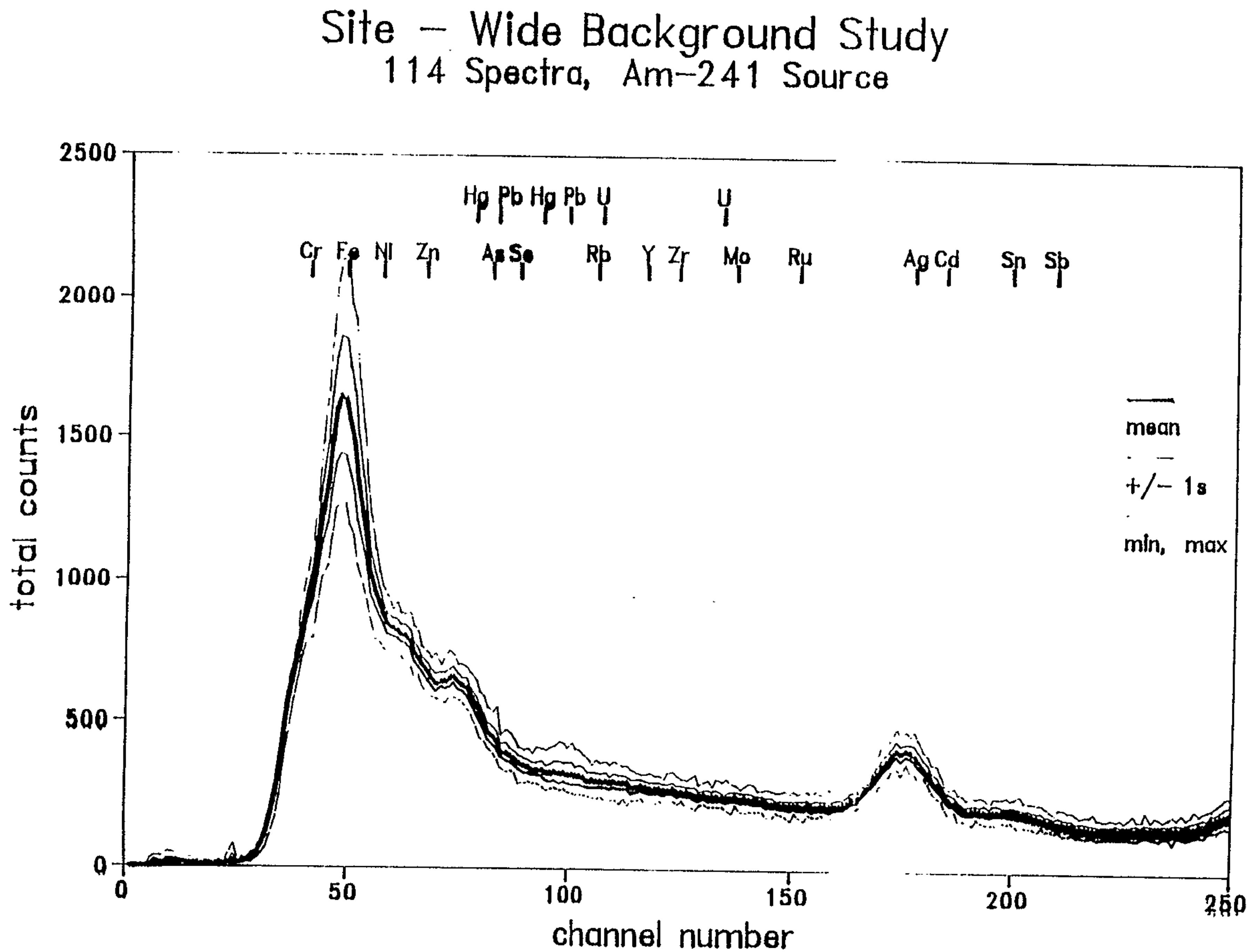
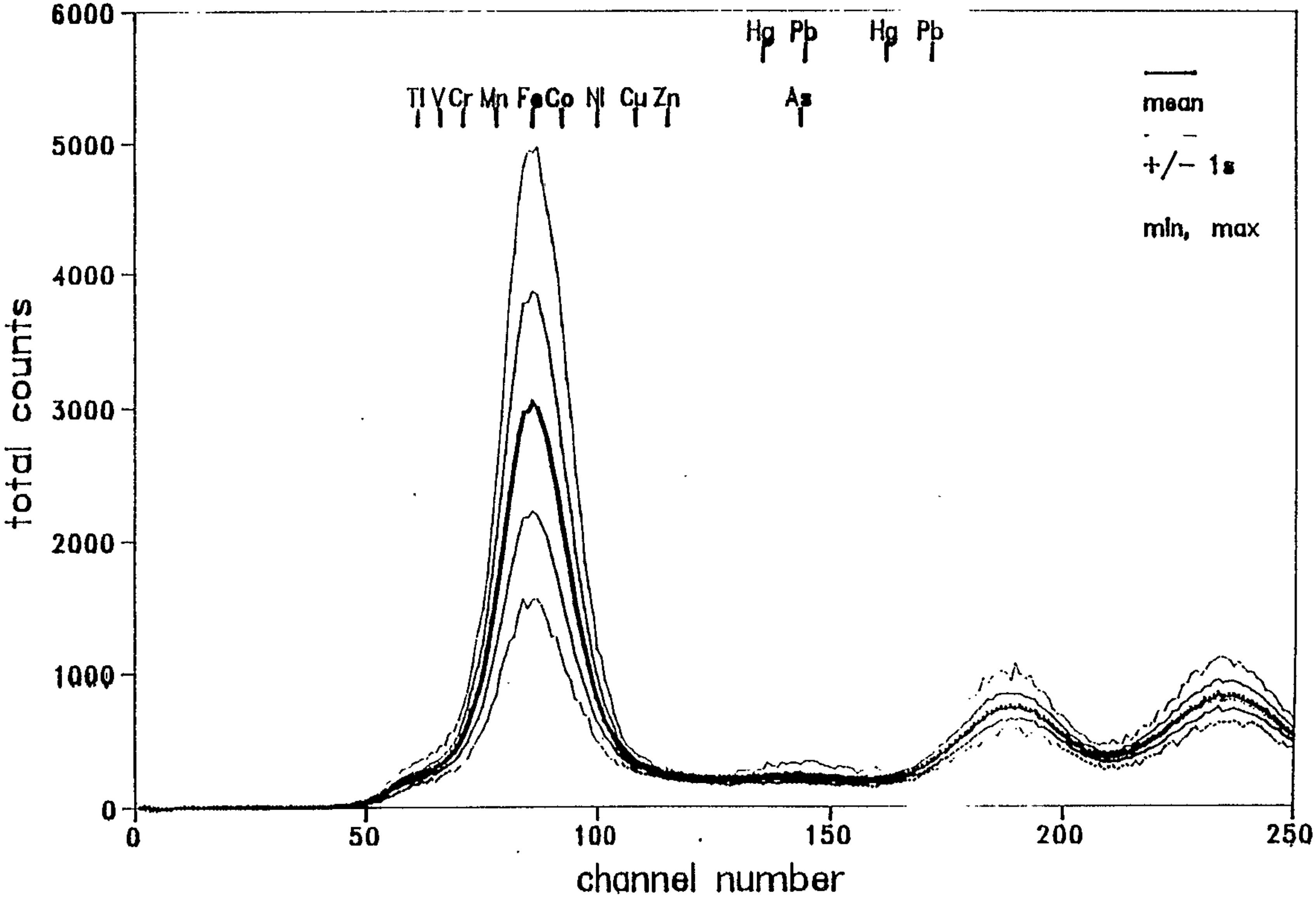
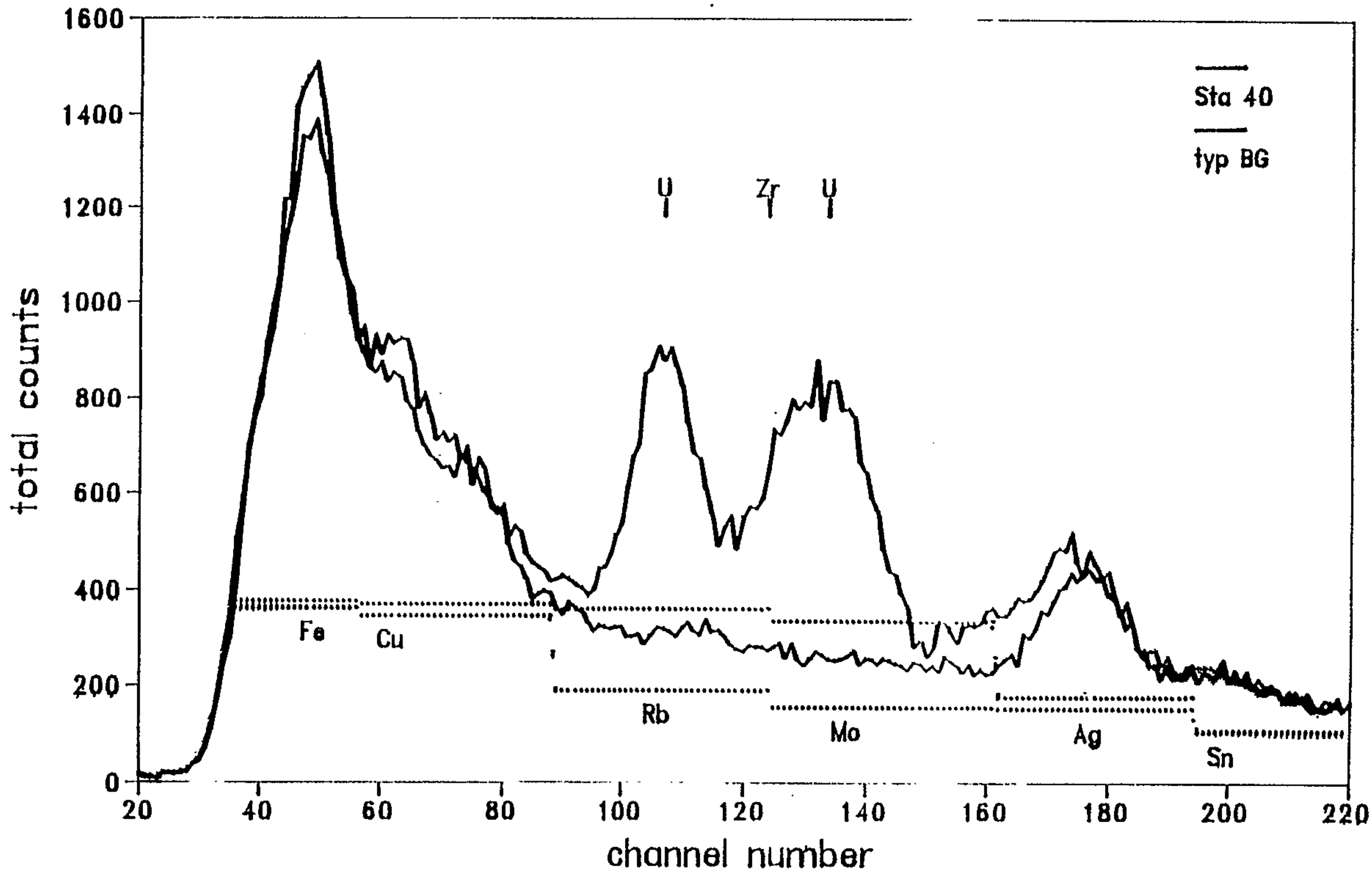


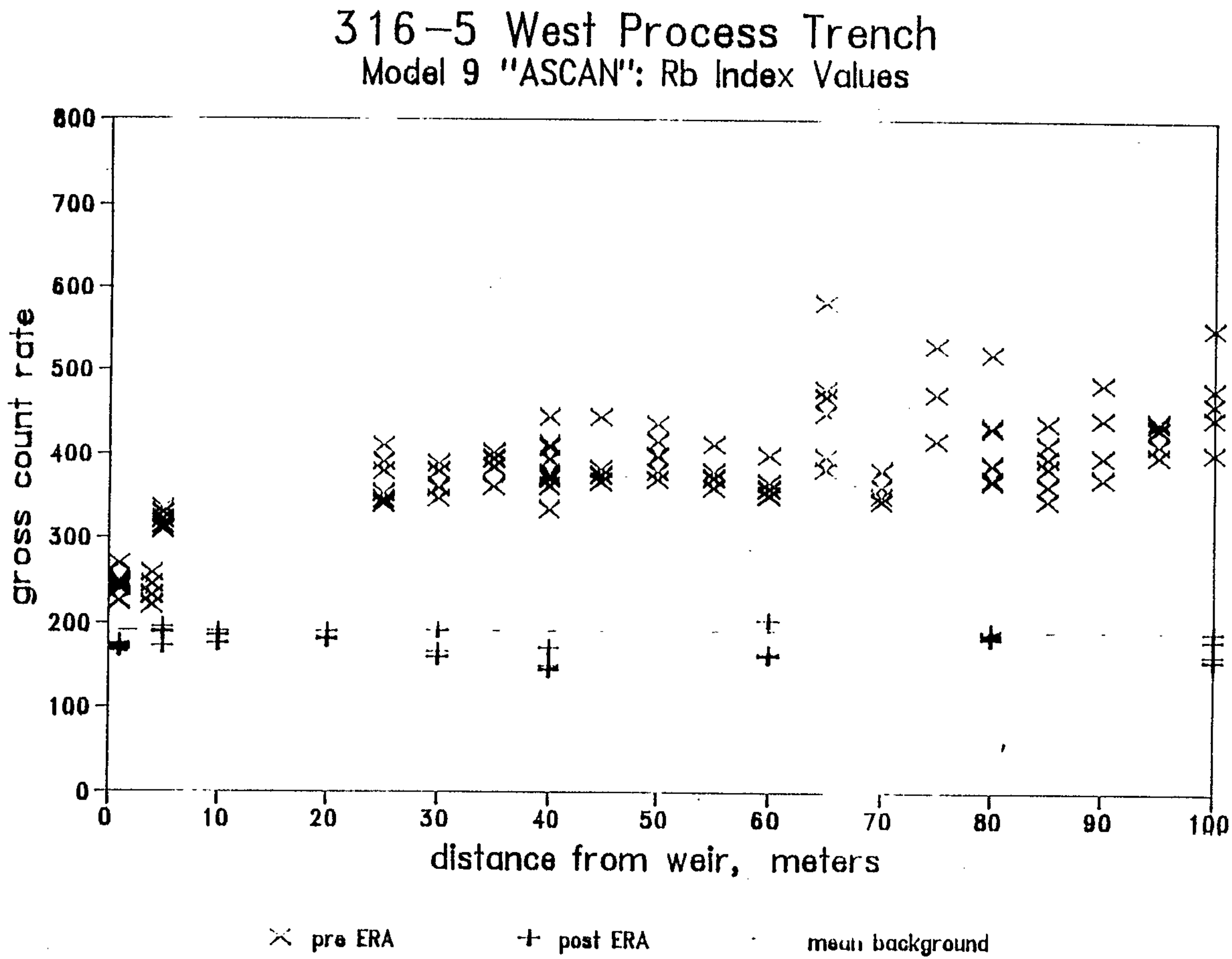
Site – Wide Background Study
114 Spectra, Cm-244 Source



316-5 Process Trenches, West Trench

In Situ XRF Spectra, Am-241, 60 sec





316-5 West Process Trench
Model 9 "ASCAN": Rb Index Values
gross count rate
800
700
600
500
400
300
200
100
0
0
10
20
30
40
50
60
70
80
90
100
distance from weir, meters
pre ERA
post ERA
mean background

9 3 1 2 7 6 3 1 0 9 4